NOTE

Valorization of Loads Petroleum by Thermal Process

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This study was performed to allow the study of the chemical composition influence of the coking process load on the efficiency and the quality of coke. For this reason, the coking of the following loads was realized: Atmospheric residue, vacuum residue and catalytic residue of cracking. As the oil residues are rich for their strongly polar composition, such as the asphaltene resins and complex structures units, which has a role in the formation of coke and as the dispersion of these latter improves the quality of coke, a study on the stability of aggregation was carried out by the addition of one stabilizer (oil extract) in the coking process load. The compounding (extracted from/ the residue of cracking oil) has been drived to the best efficiency of coke.

Key Words: Coking, Oil residue, Dispersant, Aggregation stability.

The coking of the oil residues consists of the decomposition by the delayed coking process or by fluidized bed coking[1]. The units of coking are generally biased by heavy residues, such as: vacuum residue, catalytic residue of cracking, residue of breaking and asphalt or extracted from lubricating oils[2,3]. Coking develops these oil residues, produces: Gas: they consist of a fuel gases used as fuel in the unit of coking, or sent after washing towards fuel gases of the refinery. Naphtha: light naphtha, after a hydro-processing is sent to the pool gasoline, heavy naphtha constitutes a catalytic load of reforming. Distillates: the light distillate, after a hydro-processing is sent to the pool gas oil of the refinery and heavy distillate is used like charges with FCC, in mixture with the products of distillation[4]. Coke: several types of coke can be produced: coke sponges (Sponge coke), needle coke (Needle coke), coke with balls (shot coke) and combustible coke[5].

The use of coke is directed according to the quality of this latter. The four aspects which affect the quality and the price of coke are: (i) sulphur content, (ii) content of metals, (iii) hardness and (iv) physical structure[4].

The best quality of coke is used for the manufacture of the anodes, the production out of aluminum or of the electrodes for the production out of steel, is the needle coke, which must be calcinated before its use[2].

The parameters influencing the quality and the efficiency of coke are: the nature of the load and operating conditions of the coking process[6].

The main objective of this study consists of the realization of a coking (thermal decomposition) of the oil residues for: (i) To produce a coke of a precise quality. (ii) To optimize the load which gives the best efficiency, by coking of various compounding (oil extract/residue). (iii) Valorization of its residues by recovery of a distillate and gasoline of characteristics defines.

A coking of the following loads has been realized: RAT of Hassi Messaoud's refinery, RSV of Arzew's refinery of, RCC of Adrar's refinery. (Analysis SARA of the residues is represented in Table-1). The coking process is carried out at a temperature of 500 ºC and the calcinations of coke at 550 ºC according to Fig. 1. 1. Steel reactor of 76 mm diameter and 150 mm height. 2. Gas control. 3. Electric oven. 4. Temperature control. 5. The drill (to detect the reactor temperature). 6. Receipt flask of the liquid products. 7. Gas toward the atmosphere. 8. Manometer.

The products of the coking process are: gas, distillate and coke. We will recover the gasoline from distillates of the coking process by atmospheric distillation.

The following order shows a decreasing tendency of the coke formation during the thermal processing: Asphaltenes > resins > aromatic compounds > olefin > naphtenes > light paraffin.

According to the activation of formation energy of coke[7,8]. The residue of catalytic cracking gives the best coke efficiency of 36 %. SARA Analysis showed a low content of resin in the different loads of coking (Table-1).

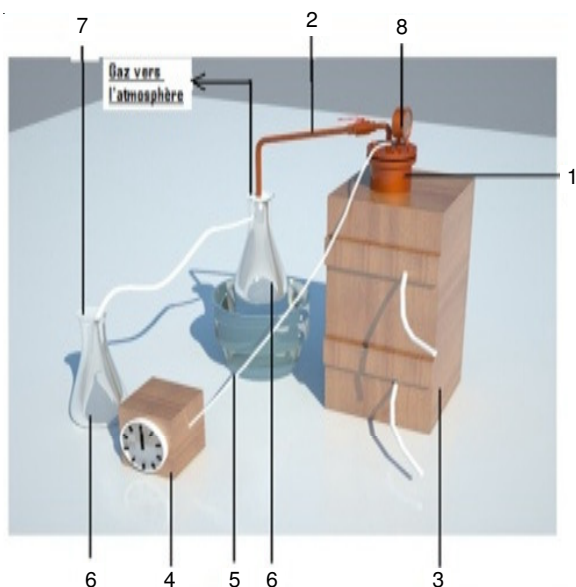| TABLE-1 ANALYSIS OF SARA'S COKING PROCESS LOADS			
Mass (%)	Satires	Aromatic	Resins
RAT	73.259	19.805	6.936
RSV	49.274	41.025	9.701
RCC	23.336	74.689	1.975
Oil extract	27.134	71.288	1.578

Fig. 1. Installation of the coking process

Therefore the principal factor which influences the coke formation is the content of aromatic. Such as the residual of cracking which is composed of 74.689 % of aromatics. To orient the deposit of the SCU and to avoid their deposit blocks during the formation of coke, it was performed a compounding of residual of cracking/oil extract, the coke efficiency is represented in figure.

Aggregation stability study: The principle of this method is to determine the stability of asphaltenes and the complex unit structures (SCU) in the catalytic cracking residue by the addition of a dispersing agent by measuring the absorptance in UV/visible according to the report/ratio (residue/dispersant).

In test tubes we will vary the volume of the residual of cracking according to the volume of the oil extract, we all respect the fact that the total volume is of 1 mL. The following percentages are used: (100/0), (90/10), (80/20), (70/30), (60/40), (50/50) and (0 %/100 %) (catalytic residue of cracking, oil extract) (% mass). (i) We add in each tube 1 mL toluene and 4 mL N-heptane. We all install in a centrifugal machine, at a predefined angular speed of 4000 round/min during 10 min. (ii) We will determine the optical density (absorption) of the upper part and the lower part by the spectrophotometer's analysis, in the UV-Visible spectrophotometer[9]. (iii) The stability factor (F) can be determine by the expression.

$$\text{Stability factor (F)} = \frac{A_{sup}}{A_{inf}}$$

where: A_{sup}: absorption (optical density) of the higher phase. A_{inf}: absorption (optical density) of the lower phase.

The increase of the stability factor (F) can be explained by the stability of the asphaltene in the samples by the addition of the extract. The reduction of the stability factor (F), depends on the quantity of the extract added, such as the addition of a dispersant in the residue, acts on the stabilization of asphaltene in three ways: (all depends on the added quantity). Adsorption on the surface of the resins which envelop the particles of asphaltene and the formation of an asphaltene envelope, from where, the increase of stability factor; the dissolution of the adsorbed resins on the surface of Asphaltene, therefore the latter tend towards association, from where reduction in the factor of stability.

Analyses of produced coke: The density of the obtained cokes of compounding (oil RCC/extract) is: 2.05. A magnifying glass interconnected to software will provide images of coke, to know the physical aspect of this latter; the form the colour and porosity.

IR Analysis: The infra-red analysis (IR) on coke, showed the presence of the connections: CH, C=N, C=C, C=O and the presence of aromatic cycles and alkanes.

The structure is practically amorphous; however, there is a beginning of the structure arrangement 'crystalline', which results in a pretence of very large peaks with approximately 3.45 and 2.065 Å. We noted the presence of a compound of crystalline structure to 1.1921 Å.

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